Part 13. RADIUM-URANIUM EQUILIBRIUM AND RADIUM-URANIUM AGES OF SOME SECONDARY MINERALS

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ABSTRACT

Ten samples of carnotite and metatyuyamunite ore that contain more than 0.1 percent lead have been analyzed for uranium, Ra^{226}, and lead. Seven contain less than the equilibrium amount of Ra^{226} for the uranium present, and three are in radioactive equilibrium within the limits of experimental error. Radioactive equilibrium between U^{238} and Th^{230} is effectively established in 500,000 years, therefore the seven radium-deficient minerals have been altered within that time span. The remaining three samples have not lost Th^{230} by alteration within the last 500,000 years or Ra^{226} within the last 15,000 years. An approximate lead-uranium age can be determined from these lead-bearing minerals if they have not been significantly leached of lead or uranium.

Carnotite and metatyuyamunite that have formed on joints and fractures are low in lead (less than 0.01 percent) and appear from field relations to be of recent origin. These coatings are local concentrations formed after the water table was lowered and the deposits were oxidized. If these minerals are not now in radium-uranium equilibrium, did not contain Th^{230} and Ra^{226} at the time of their deposition, and have not been further altered by selective leaching or enrichment of radium, Th^{230}, or uranium, their time of formation can be established. Radium-uranium ages determined on five Colorado Plateau secondary minerals range from approximately 10,000 to 120,000 years.

Radiocolloids, local concentrations of radium and its daughter products, which persist for only about 15,000 years, are present in some oxidized ores.

INTRODUCTION

The primary vanadiferous uranium ores of the Colorado Plateau are characterized by their black color. Low-valence vanadium and uranium minerals as well as iron, copper, lead, and zinc sulfides, arsenides and selenides are present. Uraninite and coffinite are associated with carbonaceous materials; vanadium is present in montroseite and in vanadium silicates. Pyrite and marcasite are abundant.

Oxidation of the uranium deposits probably took place when the water table was lowered. Ores exposed to the air oxidize rapidly and a highly variable and complex mineral suite results (Part 5 of this volume). Vanadium minerals oxidize from vanadium (III) to vanadium (IV) and (V) minerals and uranium

minerals oxidize from uranium (IV) to (VI). When the uranium is in the sexivalent form it is relatively soluble and free to migrate unless precipitated by complexing with vanadium. Many samples of ore containing carnotite and tyuyamunite (or metatyuyamunite) which were formed in place give Pb^{206}/U^{238} ages comparable to the unoxidized ores because there was no opportunity for the uranium or the elements derived from the decay of the uranium to become separated. Some deposits, however, have been leached both during and after oxidation, the uranium and vanadium having migrated relative to Th^{230}, Ra^{226}, and radiogenic lead. A criterion of such movement of uranium and vanadium would be the redeposition of carnotite or metatyuyamunite on joints and fractures containing essentially no radiogenic lead. In other cases, daughter products may be moved and the uranium and the radiogenic lead remain in place. Presence of radium-uranium disequilibrium in ores oxidized in place is another measure of migration of radioactive daughter products during the past 500,000 years.

A. M. Sherwood and R. G. Milkey of the U. S. Geological Survey made the chemical analyses for uranium and lead. R. G. Rice and W. A. Peavy, Jr., of the National Bureau of Standards, and John Rosholt of the Geological Survey measured the radium content of our samples.

OCCURRENCE OF CARNOTITE, TYUYAMUNITE, AND METATYUYAMUNITE

Several distinct occurrences of carnotite, tyuyamunite, and metatyuyamunite can be observed in the field and laboratory. These occurrences are:

1. Secondary uranyl vanadates locally replace woody material such as branches and trunks of trees and "trash piles" of organic material. Some of these occurrences are very rich in uranium and samples with as much as 35 percent uranium may be obtained with little purification. Cellular structure of these woody materials is no longer visible in thin sections although in the field the general treelike shape is still evident. Age determinations by the lead-uranium method of this type of occurrence of carnotite, tyuyamunite, and metatyuyamunite as a rule give Tertiary ages but not Quaternary ages.
2. Some of the secondary uranium minerals from the Colorado Plateau impregnate clay pebbles of various sizes and shapes. These clay pebbles are of varying uranium content and some are very high grade. These occurrences, in general, give lead-uranium ages no older than Late Cretaceous but not as young as Quaternary.
3. A large portion of the secondary ore is disseminated in sandstone. These ores are believed to be the result of oxidation essentially in place accompanied or followed by some leaching. The lead-uranium ages of these samples are variable.
4. Coatings of carnotite and tyuyamunite or metatyuyamunite on joints and fractures are relatively rare and make up a very minor amount of the secondary uranium ores of the Plateau. The geologic evidence indicates they are of Quaternary age.

RADIUM-URANIUM EQUILIBRIUM

CONDITIONS FOR EQUILIBRIUM

Radium-uranium equilibrium is established when the rates of radium formation and decay are equal. Ninety-nine percent of radium-uranium equilibrium is attained in approximately 500,000 years (Knopf, 1931, p. 110) assuming Th^{230} was not present at the time of deposition. The isotopes of uranium, U^{235} and U^{238}, decay through two series of radioactive nuclides to the radium isotopes, Ra^{223} and Ra^{226}, respectively, which in turn decay through a number of radioactive nuclides to the stable end products Pb^{207} and Pb^{206}, respectively. The contribution of the actinium series (U^{235}) to the radium content in the samples is negligible and therefore, this series will not be considered in the discussion that follows. Figure 1 is a curve of the age in years plotted against percent Ra^{226} and U^{238} equilibrium for the range 10,000 to 500,000 years.

If a uranium mineral contains less radium than required by the equilibrium ratio 3.32×10^{-7} g Ra^{226}/g U^{238}, two explanations are possible:

1. The mineral has been unaltered since deposition, and its age is less than 500,000 years.
2. The mineral has been influenced by selective leaching of Ra^{226}, Th^{230}, or enrichment of uranium, or all three, and the radium-uranium age of the mineral is indeterminate but the leaching or enrichment has taken place within 500,000 years.

Only those samples with essentially no radiogenic lead can be given meaningful radium-uranium ages, for the absence of such lead is the clue that uranium in these samples has migrated away from its former location. In addition it must be assumed that all the Th^{230} and Ra^{226} present has been produced since the redeposition of the uranium. Finally, the geologic evidence for lack of post-mineral leaching must be established. In pyritic environments uranium ores can also depart from equilibrium in the direction of a large excess of radium caused by preferential leaching of uranium (Phair and Levine, 1953, p. 358). However, to the authors' knowledge large excesses of radium are uncommon in the various occurrences of secondary minerals from the Plateau, suggesting that this type of alteration is unusual.

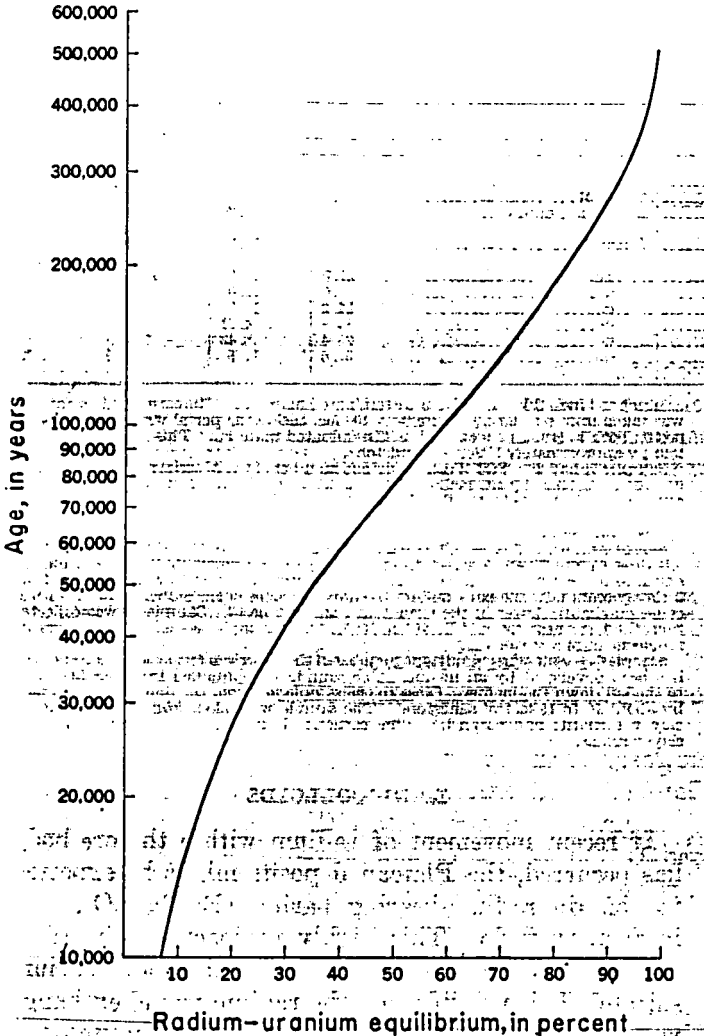

FIGURE 47.—Age in years as a function of percent radium-uranium equilibrium.

PREVIOUS WORK

In the study of the variation of the radium-uranium ratio in minerals other than pitchblende, Boltwood (1904, 1908) and McCoy (1904, 1905) found that carnotite did not show any abnormalities. Mlle. Gleditsch (1911) and Marckwald and Russell (1911a, p. 771; 1911b) found, however, that small samples of carnotite were appreciably deficient in radium.

Lind and Whittemore (1915) have published the only detailed study of the radium-uranium ratio in Colorado Plateau carnotite. They found that in samples of a few hundred pounds to several tons the ratio was in agreement with that of pitchblende, whereas small samples of a few pounds or less exhibited abnormal ratios. In one small sample the ratio was 25 percent deficient and in another 39 percent in excess of the normal ratio for pitchblende. The fact that abnormal radium-uranium ratios, both high and low, occurred in samples representative of small quantities of ores, and that all samples from bulk specimens of ores showed normal radium-uranium ratios, was interpreted as an indication of local reconcentration of radium within the ore body rather than removal of the radium by leaching.

RADIUM CONTENT OF UNOXIDIZED URANIUM ORES

It is reasonable to expect that samples of massive, unleached uraninite would be essentially in radium-uranium equilibrium. At the present time, however, only two samples of unoxidized Colorado Plateau uraninite have been examined indirectly for their radium-uranium ratio. Senftle, Stieff, Cuttitta, and Kuroda (1957) have determined that the Ra^{223}/Ra^{226} activity ratio for samples of uraninite from the Happy Jack mine and Mi Vida mines, San Juan Co., Utah to be 0.048. This agrees with the value of 0.048 for the Ra^{223}/Ra^{226} activity ratio determined by Kuroda for Great Bear Lake uraninite which is in radioactive equilibrium. For samples of secondary minerals from the Colorado Plateau, Kuroda (1954, p. 10) determined Ra^{223}/Ra^{226} activity ratios of from 0.0441 to 0.131. He interpreted this variation as a variation in the U^{235}/U^{238} ratio. However, mass spectrometric analyses of the uranium present in a selected group of secondary Colorado Plateau samples do not show any variation greater than 0.8 percent in the U^{235}/U^{238} ratio (Senftle, Stieff, Cuttitta, and Kuroda, 1957). The variation in the Ra^{223}/Ra^{226} activity ratio is here interpreted to be the result of recent preferential leaching of daughter elements during oxidation and is a consequence of the relatively shorter time required for Ra^{223} compared to Ra^{226} to return to radioactive equilibrium.

RADIUM CONTENT OF OXIDIZED URANIUM ORE

Of the 10 samples of oxidized uranium ore tabulated in table 1 containing more than 0.1 percent lead, 7 are deficient in radium when compared with the equilibrium amount. Three of the samples are in equilibrium within experimental error. As these 10 samples contain radiogenic lead they should not be dated by the radium-uranium method. These radium analyses are consistent with those reported for small samples by Lind and Whittemore (1915) and those reported by Gleditsch (1911).

As a rule, the near-surface occurrences of metatyuyamunite and carnotite have the greatest radium deficiencies. However, even samples collected from underground occurrences may show large radium deficiencies. For example, samples from the Club mine (Nos. 61, 62, and 63) were collected within 30 feet of each other and have essentially the same Pb^{206}/U^{238} age of about 70

TABLE 1.—*Radium-uranium content of some high-grade lead-bearing carnotite and metatyuyamunite samples*

Sample No.	Type of occurrence [1]	Locality	Mineral	Average U (percent)	Theoretical g Ra/g sample [2] ($\times 10^{-6}$)	Experimental g Ra/g sample [3] ($\times 10^{-6}$)	Percent radium-uranium equilibrium
9	2, 3, 4	Monument No. 2 mine, Apache County, Ariz.	Metatyuyamunite	37.9	12.6	7.62	60
13	2	Jo Dandy mine, Montrose County, Colo.	Carnotite	31.1	10.3	8.53	83
19	2, 3	Radium No. 6 mine, San Miguel County, Colo.	Metatyuyamunite	21.7	7.20	7.36	2
20	2, 3	do	Carnotite	32.6	10.8	11.3	excess 5
25	2	Calamity No. 13 mine, Mesa County, Colo.	do	32.5	10.8	10.6	excess 98
28	2	do	do	36.0	12.0	11.1	92
61	2	Club mine, Montrose County, Colo.	do	32.2	10.7	8.64	81
62	1	do	do	14.8	4.91	1.78	36
63	2	do	do	25.4	8.43	7.19	85
64	2, 3	Bob Tail mine, Montrose County, Colo.	do	34.6	11.5	8.45	73

[1] These numbers refer to the numbers given under the heading "Occurrence of carnotite, tyuyamunite, and metatyuyamunite" on p. 152.

[2] Computed from g Ra/g U in equilibrium = 3.32×10^{-7} g Ra/g U.

[3] Prepared for analysis by R. G. Rice and counted under direction of L. S. Stockman, National Bureau of Standards.

Sample 9.—Shinarump member of the Chinle formation. The sample was collected from a freshly blasted face of the open cut. The tyuyamunite and metatyuyamunite are found as coatings on the joints and fractures, as disseminated material in the sandstone and conglomerate, in thin veins of very pure material, and as tyuyamunite and metatyuyamunite replacements of clay pebbles. The sample was covered by a minimum of 6 to 10 feet of sandstone and probably was protected from extreme weathering.

Sample 13.—Salt Wash sandstone member of the Morrison formation. Sample 13 was taken from a small pocket of very high grade carnotite with corvusite approximately 140 feet inside the portal of the lower haulage adit. The field relations of sample 13 strongly suggest that the mineralizing solutions were controlled by a small joint. In comparison to the Jo Dandy mine sample given in table 2, this sample is well protected from the effects of weathering.

Samples 19 and 20.—Salt Wash sandstone member of the Morrison formation. Sample 19 was collected from a pillar at the mine portal and should be representative of the effects of moderate weathering. The metatyuyamunite occurs as a clayey seam as much as 1 inch thick and also as disseminated material. The carnotite in sample 20 was taken from a pillar approximately 100 feet inside the portal where the carnotite occurs both in small pockets and as disseminated material. This sample was overlain by approximately 30 feet of sandstone.

Samples 25 and 28.—Salt Wash sandstone member of the Morrison formation. The deposit is reached by an incline. Sample 25 was collected from a clayey seam of carnotite in the back of a small drift approximately 25 feet from the foot of the incline. Sample 28 was taken from another clayey seam in the back of a stope approximately 160 feet from sample 25.

Samples 61, 62, and 63.—Salt Wash sandstone member of the Morrison formation. All three samples were collected from a small stope approximately 200 feet from the entrance to the upper workings of the mine. Samples 61 and 63 were collected from a clayey seam near the back and on the opposite sides of the stope. Sample 61 was collected slightly lower in the formation than sample 63. Sample 62 was collected from the back near the middle of the stope. This sample seemed to be a carnotite replacement of a crushed log.

Sample 64.—Salt Wash sandstone member of the Morrison formation. The deposit has been developed by an incline. The sample was obtained from the first drift to the left down the incline. Close to the sample location, the deposit was overlain by about 10 to 15 feet of sandstone. The sample was taken from a rich pocket of clayey carnotite and corvusite. The carnotite is disseminated or occurs in thin clayey seams.

million years. Their radium-uranium equilibrium ranges from 36 to 85 percent. Such deficiencies are believed to be the result of preferential leaching processes which have removed either radium or its longer half-lived radioactive parent, Th^{230}. The differences in radium deficiency may reflect relative accessibility of the samples to the leaching solutions.

In summary, the radium-uranium equilibrium of carnotite and metatyuyamunite, which occur as replacements of woody material or as impregnations of clay or as disseminations in sandstone, is variable and is probably related to the habit and to local geologic factors such as distance from the surface of the ground and porosity and permeability of the surrounding rock. On the other hand, the deposition of crystalline carnotite and metatyuyamunite on joints and fractures is recent and the lack of radioactive equilibrium may be a result of the short time that has elapsed since the formation of the minerals.

In recent work Garrels and others (Part 15 of this volume) give a comparison of the uranium and equivalent uranium determinations for specimens from a channel sample from the Mineral Joe mine. These measurements show general agreement for each sample indicating that the channel sample is in radioactive equilibrium in spite of marked differences in extent of oxidation from sample to sample. This is evidence supporting the conclusion that uranium or radium has not been leached from the channel sample.

RADIOCOLLOIDS

If recent movement of radium within the ore body has occurred, the Plateau deposits might be expected to contain radium-bearing barite, $(Ba,Ra)SO_4$, and, in fact, they do. This highly radioactive mineral is formed by the coprecipitation of radium and barium sulfate. It is possible that the radium would exchange with the barium in barite as it moved through the sandstone in the ground waters so that these radiocolloids might actually be formed more or less continuously. Unless continuously deposited, radiocolloids—local concentrations of radium—would be apparent for only about 15,000 years after formation because of the relatively short half-life of radium^{226} (1,620 years). These radiocolloids are additional evidence, therefore, of a recent alteration of the radioactive equilibrium.

RADIUM CONTENT AND RADIUM-URANIUM AGES OF SECONDARY URANIUM MINERALS

The calculated radium-uranium ages for four samples of carnotite and metatyuyamunite from the Colorado Plateau containing less than 0.01 percent Pb determined by the Geological Survey together with the earlier result of Hess and Foshag are given in table 2. These samples are carnotite or metatyuyamunite. Their ages range from 10,000 to 120,000 years. The spread in ages from 10,000 to 120,000 years is real providing that there has been no postmineralization leaching and no Th^{230} or Ra^{226} was deposited with the sam-

TABLE 2.—*Radium-uranium content and radium-uranium ages of some high-grade carnotite and metatyuyamunite containing less than 0.01 percent lead*

Locality	Mineral	U (percent)	Theoretical, g Ra/g sample ($\times 10^{-7}$)	Experimental, g Ra/g sample ($\times 10^{-7}$)	Percent radium-uranium equilibrium	Ra/U age
Parco mine, Yellow Cat group, Grand County, Utah	Carnotite	[1] 27.2	9.03	[2] 2.60	29	40,000
Jo Dandy mine, Montrose County, Colo.	Metatyuyamunite	[1] 20.0	6.64	[3] .461	7	10,000
May Day mine, Mesa County, Colo.	do	[3] 52.0	0.173	[4] .108	62	105,000
Small Spot mine, Mesa County, Colo.	do	[3] 56.6	0.184	[4] .0333	18	24,000
Bridger Jack Flat, Cane Springs Pass, Utah [5]	Carnotite	54.6	0.186	.1244 .1269	67	120,000

[1] Average of four determinations: two by L. R. Stieff, M. N. Girhard, and T. W. Stern, U. S. Geological Survey, and two by W. A. Peavey, Jr., National Bureau of Standards.
[2] Analyst: R. G. Rice, National Bureau of Standards.
[3] Analyst: A. M. Sherwood, U. S. Geological Survey.
[4] Analyst: John Rosholt, U. S. Geological Survey.
[5] Hess, F. L., and Foshag, W. F., 1927, Crystalline carnotite from Utah: U. S. Nat. Mus. Proc., v. 72, art. 12, p. 1–6.

Parco mine.—Salt Wash sandstone member of the Morrison formation. The sample was collected from coatings of carnotite found on the surface of joint blocks at the entrance to the mine and from blocks of sandstone found on the mine dump.

Jo Dandy mine.—Salt Wash sandstone member of the Morrison formation. This sample was taken from a completely unprotected outcrop of very friable mineralized sandstone in an open cut leading to the lower haulage adit of the mine.

May Day mine.—Salt Wash member of the Morrison formation. The sample was taken from a joint surface at the portal of the mine. This metatyuyamunite formed on gypsum and was coarsely crystalline.

Small Spot mine.—Salt Wash sandstone member of the Morrison formation. This sample of coarsely crystalline metatyuyamunite had formed on gypsum which filled a fracture in the sandstone. The sample was found in the ore bin and no information concerning its exact location within the mine is available.

Bridger Jack Flat.—Salt Wash sandstone member of the Morrison formation. Hess and Foshag (1927) describe this sample, thus: "The mineral formed compact crusts one to two millimeters thick and 15 to 20 centimeters broad on the walls of narrow cracks. Where the crusts did not entirely fill the cracks the exposed surface had a dull greenish color and showed indistinct crystal terminations."

ples. If uranium has been leached from these carnotite and metatyuyamunite samples, the measured radium-uranium age would be older than the actual age of the mineral. Hess and Foshag (1927) found that crystalline carnotite from the Bridger Jack Flat, Cane Springs Pass, Utah, is 32 percent deficient in radium. The radium-uranium age of this material, using the currently accepted time required to reach radium-uranium equilibrium is approximately 120,000 years. The young ages are apparently a result of Quaternary deposition of carnotite and metatyuyamunite after the water table was lowered and the deposits oxidized. The field relations also strongly indicate that these joint and fracture coatings have been recently deposited and are related to the present erosion surface. The source of the metals in those secondary coatings was the unoxidized vanadium and uranium ores whose age is thought to be not greater than 75 million years (Stieff, Stern and Milkey, 1953, p. 1; Stieff and Stern, 1952). These Quaternary ages give the approximate time for the oxidation of the particular deposits.

These Quaternary ages were determined on local reconcentrations of carnotite and metatyuyamunite which formed after the water table was lowered and the deposits were oxidized; the ages give a minimum time for oxidation of the particular deposits.

SUMMARY

Methods of determining the time of Quaternary alteration of the oxidized Colorado Plateau uranium ores are here suggested. First, there is a group of uranium ores which appear to have been oxidized in place. These ore samples contain significant amounts of radiogenic lead yet they are not in radium-uranium equilibrium. It is assumed that these samples were in radium-uranium equilibrium until oxidation and Quaternary leaching selectively removed some of the radium or thorium^{230} present. The time at which the selective leaching took place cannot be calculated from the radium deficiency. However, the fact that radium-uranium equilibrium has not been reestablished sets an upper limit of approximately 500,000 years for this leaching process. This disequilibrium can also be explained by the recent addition of uranium but this explanation in the case of the Plateau ores is not believed likely.

Secondly, uranium essentially stripped of its daughter products has been redeposited on joints and fractures as coatings of metatyuyamunite and carnotite. These coatings contain only trace amounts of lead and are not in radium-uranium equilibrium. Assuming that the Th^{230} and Ra^{226} present have been produced since the formation of the minerals, the radium-uranium ages calculated from their disequilibrium range from 10,000 to 120,000 years. These ages indicate that some Quaternary redistribution of the uranium in the Colorado Plateau deposits has occurred after their oxidation. Finally, local concentrations of radium sulfate coprecipitated with barium sulfate are present in some oxidized deposits. These concentrations of radium are apparent for only about 15,000 years after their formation because of the relatively short half-life, 1,620 years, of radium^{226} and are another indication of Quaternary alteration of the uranium deposits.

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